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THE PHYSICAL CHEMISTRY OF THE CRYSTALLIZATION AND MAGMATIC DIFFERENTIATION OF IGNEOUS ROCKS

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(Continued from page 649 of Vol. XXIX)

V

THE INFLUENCE OF PRESSURE

A

The dependence of the melting point on uniform¹ pressure is designated, as is well known, by the formula established by Clausius-Chapeyron:

$$\frac{\Delta T}{\Delta P} = 10.333 \cdot \frac{T(v_{\text{liquid}} - v_{\text{solid}})}{E \cdot q},$$

$\frac{\Delta T}{\Delta P}$ designating the alteration of the melting point in C° per increase of atmospheric pressure, T the melting point in absolute temperature (starting from -273°), q the latent melting heat in gr. cal. pr. gr., v the specific volume (in cm³ per gr.) at the melting point— $v_{\text{liq.}} - v_{\text{sol.}}$ accordingly meaning the difference of specific volume between the liquid and the solid phase at the melting point—and $E = 425$.

In by far the most substances $v_{\text{liq.}} - v_{\text{sol.}}$ is positive at common and at moderate pressures. Accordingly the minerals, when melting, must, as a general rule, expand in volume or become of lower specific gravity. The case is entirely the reverse of that of ice and of bismuth.

¹ Within a liquid, such as a magma, also in the case that more or less mineral has already crystallized, the pressure always becomes uniform or hydrostatic, and in this case the formula quoted is applicable. Quite different is the case of *non-uniform* compression (and stress) in the solid phase. I beg to refer to a series of publications of recent years (see the review of John Johnston in this Journal, XXIII [1915], p. 732).

G. Tammann, as is well known, has pointed out that for many salts, $v_{\text{liq.}} - v_{\text{sol.}}$ decreases with increasing pressure so that, when the pressure is extraordinarily high, for instance 5000–10,000 atmospheres, it approaches zero; at still higher pressure the difference may be negative. However, this is not the case of substances in general. Thus P. W. Bridgman¹ has experimentally ascertained that, in a great many substances (metals and some salts, etc.), on pressures rising to 12,000 atmospheres (corresponding, for a magma, to a depth of about 40 kilometers), $v_{\text{liq.}} - v_{\text{sol.}}$ remains positive—indeed with gradually (somewhat) decreasing magnitude for increasing pressure. Some substances, even at the enormous pressures just mentioned, show but an inconsiderable decrease of the difference of volume, and J. Johnston and L. H. Adams² showed, for a number of metals, under a pressure of up to 2000 atmospheres (corresponding, for a magma, to a depth of about 7.5 kilometers), a rectilinear course of the difference of volume.

Under a pressure of one atmosphere all the silicate minerals hitherto examined show, at room-temperature, a lower specific gravity for the glass, that is the extreme viscous fluid phase, than for the crystalline, that is the solid phase.

According to what we have stated above, we must take it for granted that for rock-forming minerals $v_{\text{liq.}} - v_{\text{sol.}}$ is in all cases positive, and that the difference of volume existing for a pressure of one atmosphere will remain nearly constant, at any rate down to depths of a few kilometers, and that even to depths of 5 or 10 kilometers it will show practically no or only a little decrease.

As far as the common rock-forming silicate minerals are concerned, the *latent melting heat* is very high throughout. In fact for minerals melting at about 1200° to 1400° or 1500°, it amounts to about 90 or 100 gr. cal. pr. gr.—for some a little more and for some a little less.³

¹ *Proc. Amer. Acad.*, XLVII (1911–12) and *Physic. Rev.*, III (1914).

² *Zeits. f. anorg. Chemie*, 72 (1911), and *Amer. Jour. of Sci.*, XXXI (1911).

³ As for anorthite (melting point 1550°), diopside (1391°), åkermanite (about 1310°) and fayalite (about 1075°), I have in earlier publications (*Silikatschmelzlös.* II [1904], with correcting calculation in my publication on slags in Doelter, *Handb. d. Mineralchemie*, I [1912], p. 942) determined the latent melting heat at respectively about 105, 94, 90, 80 cal., with an error limit of ± 15 or 20 cal. For anorthite Bowen

Thus the divisor of the formula becomes very great, and consequently the melting point of the silicate minerals rises but very little on increasing pressure.¹ As an illustration I cite a case treated in my publication just quoted:

For a mineral with melting point = 1200° , melting heat = 100 cal., density in the solid phase = 3.000 and in the fluid phase = 2.887, $v_{\text{liq.}} - v_{\text{sol.}}$, at the melting point accordingly amounting to 0.013 or 3.9 per cent we calculate the melting point at higher pressures:

Pressure	Depth below the Surface	Melting Point
1 atmosphere.....	0 kilom.	1200°
270 atmospheres.....	1 kilom.	1201.3°
2700 atmospheres.....	10 kilom.	1213.5°
10,000 atmospheres.....	37 kilom.	1250°

We have assumed, in this instance, in accordance with an early examination carried out by C. Barus,² a percentage value of 3.9 per cent, for the difference (at the pressure of one atmosphere) between the specific volume in the fluid and in the solid phase of the melting point, and we assume also the same value at higher pressure.

A series of determinations of glass and of crystalline substance at room-temperature (15° or 20°) show, for rock-forming minerals and for rocks, the following percentage differences of specific volume:³

In some cases only about 3 per cent (2.9–3.5 per cent), in most cases between 5 and 8 per cent, exceptionally up to 10.6, 11.4, and in a single case 13.6 per cent.⁴

(in his study on plagioclase, *loc. cit.*) has calculated 104.2 cal. (I found 105 cal. $\pm$ 20 per cent.) For diopside W. P. White (*Amer. Jour. Sci.*, XXVIII [1909], p. 486, footnote), according to a preliminary determination, states 106 ± 15 cal. (I found 94 ± 15 per cent.)

¹ I beg to refer to my statement in *Tscherm. Mitt.*, XXVII (1908).

² *Phil. Mag. London*, XXXV (1893), and *U.S. Geol. Surv. Bull.* 103.

³ Most of these statements are grouped from Doelter, *Handb. d. Mineralchemie*, I (1912), p. 672.

⁴ The last named value concerns CaMgSiO_6 with density of the mineral diopside = 3.275, and of the glass = 2.830 (Allen, White, etc., *Amer. Jour. of Sci.*, XXVII [1909], $v_{\text{liq.}} - v_{\text{sol.}}$ accordingly = $0.3533 - 0.3053 = 0.048$).

These figures, however, cannot be transferred so as to be applied at the melting point without being corrected, as the crystalline and the glassy phase will, as a general rule, differ a little as to volume dilation.

The only precision investigation known to me of the specific volume of a silicate at the melting point, has been carried out by A. L. Day, R. B. Sosman and J. C. Hostetter,¹ who determined for a diabase:

At 20° in the crystalline phase dens. = 2.975 (specific volume = 0.3362) and in the glassy phase dens. = 2.763 (specific volume = 0.3620), the percentage difference at 20° accordingly, amounting to 7.1 per cent, the glass being taken as the starting point.

This percentage difference increased at the melting point to 9.1 as a minimum and 10.9 as a maximum, and next to the last figure, accordingly to about 10.5 per cent corresponding to a difference = ca. 0.041 of the specific volume.

From what we have stated above, we take it for granted that, at the melting point of the common rock-forming minerals (melting at about 1200–1500°), $v_{\text{liq.}} - v_{\text{sol.}}$ will, as a general rule, vary between the limits of about 0.015 and 0.045. Assuming a melting heat of 100 cal. and a melting point of respectively 1200° and 1500°, we shall have, for a pressure of 1000 atmospheres, corresponding to a depth of about 3.7 kilometers, a rise of temperature of respectively about 5–6° and about 15–18°. That is to say, in igneous flows, at depths of up to 0.5 or 1 kilometer, the melting point of the different minerals only rises between about 1° and about 4 or 5°, while in deep-seated rocks, in which the crystallization takes place at depths of 5, 10, or 15 kilometers, there may be involved a rise varying respectively between about 6° and 30°, between about 12° and 40°, and between about 15 or 20° and 60°.

Thus, even in deep-seated rocks crystallizing at very great depths, the rise of the melting point is rather inconsiderable. And it should be particularly emphasized that the *difference* of rise of the melting points of the various minerals crystallizing in one and the same magma, will only amount to some few degrees; even in deep-seated rocks the difference is rather small, in fact rarely amounting to more than 10, 20, or perhaps in some cases 40°.

¹ *Amer. Jour. of Sci.*, XXXVII (1914).

As to the *dislocation of the eutectic* by uniform pressure, H. W. Bakhuys Rooreboom¹ has stated that in this case also the formula of Clausius-Chapeyron is applicable. The rise of temperature of the binary (and the ternary) eutectic of the rock-forming minerals by pressure may consequently be measured by the same *small* measures that have just been indicated for the minerals themselves.

Moreover, it is to be noted that the tangent to the melting curve near the origo (respectively 100 per cent *a* and 100 per cent *b*) is determined by the factors: *T* (absolute temperature), *q* (melting heat), and the electrolytic dissociation which three factors are but little dislocated by pressure, and finally the molecular weight which is constant if no polymerisation takes place. In other words, the melting curve in a binary system (Fig. 50) near the origo will, at high pressure, take a course parallel to that of the melting curve at low pressure. The further course of the melting curve is also essentially determined by the constants just mentioned, which are generally very little dislocated by pressure.

This relates to the general experience that pressure has but little influence on the solubility of the mutual solutions, provided that no vapor phase is present.

The contents of *a* and *b* at the intersecting point of the curves, in other words the composition of the binary eutectic, (E_p , at low pressure, and E_{pn} at high pressure) will accordingly be but very little dislocated by pressure. And this accords with the fact that the temperature of E_{pn} , as just stated, is only very little higher than that of E_p . This reasoning can also be extended so as to be applied to the ternary and still more complex eutectics.

¹ *Heterogene Gleichgewichte*, II (1904), p. 715.

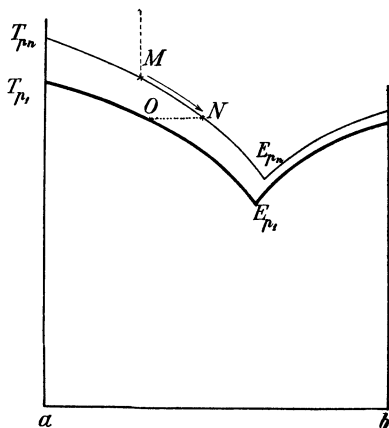


FIG. 50.—Illustrating the unessential dislocation of the composition of the binary eutectic by uniform pressure.

T_p , T_{pn} = melting point and E_p , E_{pn} = binary eutectic by respectively low and high pressure.

The error made by transferring the determination of the *composition of the eutectic on a pressure of one atmosphere*, to be applied also to the *pressure prevailing during the crystallization of the eruptive rocks*, will accordingly be *rather unimportant provided that the minerals involved are formed independently of pressure*.

I have demonstrated this fact by some petrographic instances in my publication in *Tscherm. Min. Petrogr. Mitt.*, XXV (1906), and XXVII (1908). I will here only point out that the analyses of the final eutectic quartz: feldspar-product from igneous flows,

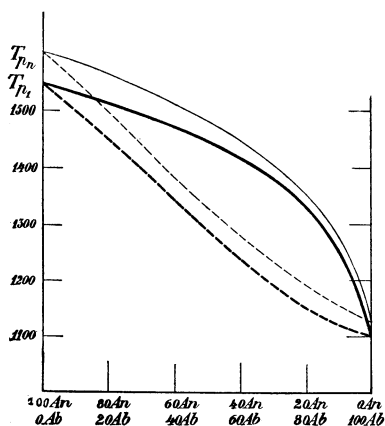


FIG. 51.—Illustrating the unessential dislocation of the *horizontal* difference between the liquidus and the solidus curve of the An:Ab-system by low and high pressure.

T_{pr} , T_{pn} = smelting point by respectively low and high pressure.

melting point and on the eutectic may be transferred, in all essentials also to *mix-crystal systems*, or at any rate, to the continuous mix-crystal systems of type I.

For example, let us consider Ab:An. Even if the melting point of An should, at high-pressure, rise a little more or a little less than of Ab, it must be presumed a priori that the course of the liquidus and the solidus curves, and, what is petrographically of the greatest importance, the *horizontal distance between the liquidus and the solidus curves*, will remain almost the same (Fig. 51) at a high pressure

formed at a comparatively low pressure, accord within the limits of error exactly with the corresponding final product from granitic deep-seated rocks and also with the graphic granite in the Archean granite-pegmatite dikes formed at very great depths (see the analysis No. 1-40). And I deem it right to employ the experimentally determined eutectic Qu:An, at a pressure of one atmosphere, for parallism with the eutectic Qu:Ab in deep-seated rocks or granite-pegmatite dikes (Fig. 3).

The same general reasoning as to the inconsiderable influence of pressure on the dislocation of the

(p_n) as at a low one (p_i). This is also verified by petrographic experience. Thus in effusives and dike-rocks with a proportion Ab:An, fixed from the analysis of the whole rock, the mix-crystal first separated had nearly exactly the same composition as in a melt of Ab+An crystallizing at a pressure of one atmosphere.¹

B

The formula of Clausius-Chapeyron quoted (p. 611) is to be applied also to the dislocation, at uniform (hydrostatic) pressure, of the *inversion point* between two reversible solid phases of one and the same substance.

The volume difference $v_1 - v_2$, in this case, involves the difference between the solid phases stable at higher and lower temperature, and the melting heat must be replaced by the inversion heat.

Also here $v_1 - v_2$ is in most cases positive, and only exceptionally negative.²

The *inversion heat* between two solid phases of one and the same substance is, so far as we now know, always positive and generally very small, sometimes low even almost to zero, and in most cases it amounts only to a small fraction of the melting heat.³

For metals, sulphides, silicates, etc., the divisor of the temperature: pressure formula thus becomes, as a general rule, very small,

¹ I refer, on this subject, to a comparison between my account in *Tscherm. Mitt.*, (1905), of the mix-crystal system Ab:An in igneous rocks and the diagram of Bowen (cf. Fig. 2, dating from 1912-13) for the Ab:An melt at the pressure of one atmosphere. The analyses of the plagioclase first separated in the rocks concern partly plagioclase somewhat zonally constructed, and partly plagioclase that has grown a little poorer in An and richer in Ab on account of partial equilibrium of the solid and the liquid phase. The plagioclase mix-crystal first separated in andesites, dacites, etc., will, accordingly, have been somewhat richer in An and poorer in Ab than is indicated in the analysis tables on pages 503 and 512 in my publication in *Tscherm. Mitt.*, XXV (1905).

² As an instance of negative $v_1 - v_2$ is mentioned: The density of the three modifications of Ca_2SiO_4 amounts to: of α (at a high temperature) = 3.27, of β = 3.28, and of γ (at a low temperature) = 2.97. The density of common stannum is = 7.3, that of the gray tin formed at a low temperature (undercooled much below $+20^\circ$) is only = 5.8. Both in the passage from β to γ - Ca_2SiO_4 , and from the common white stannum to the gray one, so great an increase of volume takes place that the substance is disintegrated by itself.

³ However, to this rule also there are some exceptions. The most striking instance is formed by lithiumsulphate having an inversion heat even five times greater than the melting heat (Hüttner und Tammann, *Zeit. f. anorg.*, Ch. 43 [1903]).

and consequently the inversion temperature, even if $v_1 - v_2$ only amounts to a medium positive value, will have a not quite inconsiderable rise on increasing pressure. And if $v_1 - v_2$ is considerable (and positive) the *rise of inversion temperature owing to pressure will be exceedingly great.*¹

This has been experimentally examined for monoclinic and orthorhombic sulphur (monocline S, on pressure of one atmosphere having its melting point at 119.25° , density = 1.98, melting heat, = 12.5 cal. 1 inversion temperature between monoclinic and orthorhombic S, on pressure of one atmosphere = 95.6° , inversion heat = 2.52 cal., density of orthorhombic S = 2.07 and melting point = 112.8°).

On pressure the inversion temperature between monoclinic and orthorhombic sulphur rises more than the melting curve of monoclinic sulphur. The two curves intersect at a pressure of 1320 kilogrammes pr. cm^2 (= 1275 atmospheres) and at a temperature of 151° , and at *still higher pressure only orthorhombic sulphur may be formed.*²

Accordingly it will not be surprising that, in the case of a rock-forming mineral which at low pressure has an α -form (at high temperature) as well as a β -form (at lower temperature), it should always be the β -form,³ or the form stable at lower temperature, that crystallizes in eruptive rocks formed at high pressure.

Let us consider particularly some of the most important modifications of SiO_2 :

The inversion from α -cristobalite into α -tridymite at $1470 \pm 10^\circ$.⁴

The inversion from α -tridymite into α -quartz at $870 \pm 10^\circ$.⁴

¹ Therefore, the doctrine, advanced by me in 1908, of the inconsiderable rise of the *melting* point of silicate minerals cannot also, as a general rule, be transferred to the *inversion* point. I refer, on this subject, to the instructive remarks, made by V. M. Goldschmidt, *Die Kontaktmetamorphose im Kristianiagebiet* (1911), p. 112, and by C. N. Fenner, *Jour. of the Wash. Acad. of Sci.* (1912), 2.

² See G. Tammann *Krystallisieren und Schmelzen* (1903), and several publications by Roozeboom reviewed in Doelter's *Phys.-chem. Mineralogie* (1905), p. 31.

³ According to the terminology used by Boeke and by many other mineralogists, I employ α to designate the modification stable at a higher temperature, β and γ to designate the modifications stable at lower temperatures. To avoid misconception, it should be noted that some investigators, among them Wright and Larsen, have employed quite the reverse terminology (α designating lower, and β higher temperature).

⁴ C. N. Fenner, *Amer. Jour. of Sci.*, XXXVI (1913).

The inversion from α -quartz into β -quartz at $575 \pm 2^\circ$.¹

According to the statement made by A. L. Day, R. B. Sosman, and J. C. Hostetter² the specific volume of β -quartz is at 20° 0.3775 (=density 2.649), but rises by heating, and at 561° , or just below the inversion point, it has risen to 0.3922. At the inversion point there is a sudden rise, which, however, is not precisely stated, and then we pass on to α -quartz at 585° with a specific volume of 0.3972.

According to the statements of F. E. Wright and Esper L. Larsen the inversion heat, when β -quartz is transformed into α -quartz, amounts to 4.3 ± 1 cal. If we set the volume difference at the point of inversion at 0.003 and the inversion heat at 4.3 cal., there is a rise of 0.015° per atmosphere, which makes at a pressure of 1000 atmospheres, corresponding to a depth of about 3.7 kilometers, a rise of about 15° . This affords a measure for the order or quantity which has to be taken into account. Accordingly the difference between α -quartz and β -quartz, if depths of more than 5 kilometers are not involved, can, at any rate with only a little modification, be employed as a geological thermometer.

As to the relation of inversion point and pressure between α -quartz and tridymite the case is quite different. At room temperature tridymite has a specific volume of 0.4329 (density = 2.31, medium of 2.282 and 2.326) and β -quartz a specific volume of 0.3775 (density = 2.649); $v_1 - v_2$ accordingly amounts to 0.0554, which is a very high value. By heating, β -quartz, as has just been mentioned, expands its volume considerably and then changes into α -quartz, which, according to the statements of Day, etc., has at 850° a specific volume of 0.3957. According to the law of the expansion of bodies by heating, tridymite also must expand its volume at higher temperature, but how much is not stated. If we estimate its specific volume at 875° at 0.445, the volume difference $v_1 - v_2$ at 875° will amount to 0.05 (or perhaps a little more).

The inversion heat is not stated, but must be supposed to be tolerably low. A rough estimate, rating the inversion heat at 10 and 5 cal., respectively, gives a rise of inversion temperature per

¹ F. E. Wright and E. S. Larsen, "Quartz as a Geologic Thermometer," *Amer. Jour. of Sci.*, XXVII (1909).

² *Amer. Jour. of Sci.*, XXXVII (1914).

atmospheric pressure of respectively 0.115 and 0.23° . A corresponding rough calculation has been made by Fenner,¹ who presumed $v_1 - v_2 = 0.057$ (as at room temperature) and inversion heat = 15 cal., which makes a rise of temperature per atmosphere of 0.105° . Starting from these figures ($15, 10, 5$ cal.) we should have, on a pressure of 270 atmospheres (or at the depth of 1 kilometer), a rise of the inversion point of respectively $28, 38$ and 76° , or from 875° to respectively $908, 913$ and 951° —and it may be that even the last number is too low an estimate. On the pressure prevailing at the depth of a few kilometers, the inversion point quite certainly will most likely prove to be considerably above 1200° .

The binary eutectics Qu:Or and Qu:Ab, at a pressure of one atmosphere, I estimate at about 1075° – 1100° , respectively 975° – 1000° . The ternary eutectic Qu:Or:Ab must lie somewhat lower, probably at about 950° or 925° .

If we choose for instance a common granite, quartz porphyry, or rhyolite, the final crystallization must here take place as a complex eutectic Qu:Or:Ab+An, with a little ferric oxide and Mg, Fe-silicate, at a pressure of one atmosphere at a temperature of presumably about 900° – 950° . And even if there occurs some surplus quartz, so that the crystallization of this mineral begins at a comparatively early stage, still the first crystallization of SiO_2 will scarcely take place at a higher temperature than 950° or 1000° . These values of temperature reckoned on the pressure of one atmosphere must certainly be increased somewhat, but only a little, for crystallization at great depth and under high pressure, but, as we shall mention later, must be decreased by the content of water, etc., especially in the granitic deep-seated magma.

As, on the other hand, the temperature of the inversion point between α -quartz and tridymite rises so considerably, SiO_2 will never crystallize in deep-seated rocks as tridymite, but always as quartz, and this quartz in granite, quartz-porphyry, and graphic granite is, as pointed out by Wright and Larsen, always an α -quartz.

Tridymite as a primary² formation in igneous rocks is, as is well known, limited to certain rhyolites, trachytes, andesites, etc.,

¹ *Jour. of the Wash. Acad. of Sci.*, 2 (1912), p. 479 and *Amer. Jour. of Sci.*, XXXVI (1913), p. 347.

² The hydrothermal formation of tridymite is here left out of consideration.

consequently to effusive rocks and to some dike rocks crystallized at a small depth. The crystallizing temperature will here have been above, probably indeed only a little above, the inversion point between α -quartz and tridymite in force at the pressure in question, and accordingly at depths of some hundred m., viz., at about 900° or perhaps a little higher.

By stating the depths at which SiO_2 , in the effusives and dike rocks here mentioned, occurs as quartz or as tridymite, our knowledge of the influence of pressure on the rise of the inversion point between α -quartz and tridymite will be increased. Fenner (*Amer. Jour. of Sci.*, XXXVI, p. 348) describes a volcanic rock in which quartz phenocrysts were first formed and were afterward transformed into tridymite. Fenner suggests the explanation that the quartz phenocrysts were formed at higher pressure a little below the inversion point in force at the pressure in question, and that the magma with its phenocrysts was afterwards brought nearer the surface, viz., to a diminished pressure, lying a little above the inversion point at the given temperature. The phenocrysts of α -quartz first formed at the greater depth must consequently now be transformed into tridymite. Fenner, however, expresses some doubt as to this explanation, which, after all, in my opinion, is the natural one.

According to what has been stated by Wright and Larsen, the quartz in the graphic-granite from granite-pegmatites was originally formed as α -quartz, and accordingly at a relatively high temperature, viz., between the inversion point between β - to α -quartz and α -quartz to tridymite. But, besides, there sometimes occurs, in the granite-pegmatites, quartz that "in all probability has never been heated above the inversion temperature between α - and β -quartz." "These large masses of quartz were in certain cases definitely stated by the field relations to be the last portions of the pegmatite to crystallize out." This β -quartz which is formed below the inversion point between α - and β -quartz, and the formation of which, at the enormous pressure, must have taken place at a temperature below 600 or 625°, must be supposed to have been separated from a particular solution of $\text{SiO}_2 + \text{H}_2\text{O}$ (see following chapter on the influence of the light volatile compounds).

According to the investigations made at the Geophysical Laboratory in Washington, the inversion point between pure $\alpha = \text{CaSiO}_3$ (*pseudowollastonite*) and $\beta = \text{CaSiO}_3$ (*wollastonite*) has been stated at about 1200° . Some amount of MgSiO_3 entering isomorphously into the silicate makes the inversion point rise; thus about 6 per cent MgSiO_3 brings about a rise up to 1300° and 17 per cent $\text{CaMgSi}_2\text{O}_6$ ($=ca.$ 8 per cent MgSiO_3) even up to $1345 \pm 10^\circ \text{C}.$ ¹ The inversion point of the mineral wollastonite occurring in the contact zones, containing as a general rule a little MgSiO_3 , must, accordingly, be estimated, at the pressure of one atmosphere, at about $1250\text{--}1300^\circ$, and at a high pressure even a little higher temperature must be presumed, though, on account of the small difference of density between the two forms, the rise will probably be quite inconsiderable.²

As will be brought out in a later paper, the *eruption* of the magmas, as a general rule, took place at a temperature which was for the deep-seated rocks almost exactly *identical with the temperature of the beginning crystallization*. For the porphyry rocks we may in many cases assume a temperature of the eruption even somewhat below that of the beginning crystallization.

If we leave out of consideration the peridotites, anorthosites, and analogous anchi-monomineral deep-seated rocks, the *eruption temperature*, accordingly, must only exceptionally have been so high as about 1300° . For many anchi-eutectic rocks, I estimate it at about 1250° , and for granitic rocks, even much lower still, as 1000° or somewhat less. Thus, it is easily explained that in the contact zones there always occurs wollastonite and never pseudo-wollastonite.

MgSiO₃.—According to the investigations made by O. Andersen and N. L. Bowen³ MgSiO_2 has, at usual pressure, no true melting point, as, at 1557° , MgSiO_2 is divided into solid Mg_2SiO_4 (forsterite) and liquid. The weight proportion of the two phases is 5.5 per cent

¹ T. B. Ferguson and H. E. Merwin, *Amer. Jour. of Sci.*, XLVIII (1919), p. 165, and the earlier investigations here cited.

² White and Larsen, *Amer. Jour. of Sci.*, XXVII (1909), p. 421; cf. V. M. Goldschmidt, "Die Kontaktmetamorphose im Kristianiagebiet" (1911), p. 110.

³ *Amer. Jour. of Sci.*, XXXVII (1914), and *Zeits. f. anorg.*, Ch. 87 (1914).

forsterite to 94.5 per cent fluid. With continued heating the forsterite dissolves in the course of time, so that all is transformed into fluid at 1577° .

On cooling a melt of MgSiO_3 , there first crystallizes (at 1577° – 1557°) a little forsterite, which on continued (and slow) cooling is resorbed under new formation of solid MgSiO_3 (at high temperature clinoenstatite).

The inversion point, at a pressure of one atmosphere, between clinoenstatite and enstatite amounts to about 1100° . The point cannot be settled exactly. The above reference to the treatise of Andersen and Bowen is for pure MgSiO_3 (at one atmospheric pressure).

For $(\text{Mg}, \text{Fe}) \text{SiO}_3$, $(\text{Mg}, ^{\text{Fe}}) \text{SiO}_3$ and FeSiO_3 , the following must be taken into consideration:

Mg_2SiO_4 has melting point 1890° .

Fe_2SiO_4 has melting point about 1100° .

For the intermediate mixtures there are intermediate melting point intervals (Fig. 22).

Fe_2SiO_4 and Mg_2SiO_4 with relation about in the middle between Mg and Fe, has a considerably lower melting point interval than 1550° , and consequently cannot be separated in the solid face at the first mentioned temperature from a $(\text{Mg}, \text{Fe}) \text{SiO}_3$ melt. This makes it probable that the splitting by one atmosphere's pressure of solid pure MgSiO_3 into olivine-mineral and fluid may be transferred to $(\text{Mg}, ^{\text{Fe}}) \text{SiO}_3$ with only a little Fe, but not to metasilicate with predominant Fe or with a middle relation between Mg and Fe.

Clinoenstatite (respectively clinobronzite), as well known, sometimes occurs in meteorites, but has never been determined certainly in terrestrial igneous rocks. If the metasilicate in the rocks originally had existed in the clino-modification (clino-enstatite, -bronzite, -hypersthene) we might, according to the experiences from the meteorites, suppose that the original mineral, in any case, occasionally would still have been in existence. But while this, as far as we know up to date, never is the case, the explanation seems to be that the crystallization of the Mg, Fe-metasilicate in the common igneous rocks—of composition between 0.08 FeSiO_3 , 0.92 MgSiO_3 and about 0.4 FeSiO_3 , 0.6 MgSiO_3 —always took place

for the existing pressure at a temperature lower than the inversion point between the clino- and the ortho-modification of the meta-silicate. This view is strengthened by the fact that in the rocks where the metasilicate has crystallized at an early stage it shows the crystallographic contour of the orthopyroxene.

It is probable that the inversion temperature between the clino- and the ortho-modification rises not quite inconsiderably with the pressure. The difference in density between clinoenstatite and enstatite is indeed very little, but if the inversion heat is minimal, as only a small fraction of 1 cal., the inversion temperature will nevertheless increase not inconsiderably with the pressure. In the common anchi-eutectic norites, etc., the crystallization interval for the most part lies at about 1275–1200°, which must be lower than the inversion boundary at high pressure between the two Mg, Fe-metasilicate stages. In bronzite rocks and bronzite-carrying olivine rocks a not inconsiderably higher crystallization interval may be presumed, but even in these rocks we cannot observe any structural indication that here originally occurred a clino-modification.

By melting MgSiO_3 at 1557° to a liquid in connection with solid olivine—the latter only in a small quantity—and at 1577° only to a liquid, $v_1 - v_2$ will, in accordance with what happens in all previously examined silicates, doubtless be positive. That is to say, the “incongruent” melting point of MgSiO_3 , in the same way as of other silicates, must be supposed to rise somewhat with the pressure. The splitting of MgSiO_3 to an olivine (very poor in FeO) in the igneous rocks might thus have taken place at a temperature somewhat above 1557°. But the crystallization of the hypersthene-bearing gabbros, syenites, granites, etc., occurred, as just mentioned, at a considerably lower temperature. The conclusion of this, according to my view, is that the proved crystallization of forsterite in a melt of MgSiO_3 at a pressure of one atmosphere cannot be transferred to take place at the crystallization of the bronzite- or hypersthene-bearing deep-seated rocks. I cannot agree with more of the opinions maintained by Andersen and Bowen (*loc. cit.*) and Bowen¹ since these investigators have not taken into consideration the influence of pressure.

¹ The crystallization of haplobasaltic and haplodioritic magmas (1915), and The later stages of the evolution of the igneous rocks (1915).

As an argument for the primary crystallization of olivine with following resorption of olivine under new-formation of orthopyroxene, several investigators have referred to the well-known kelyphitic or coronation zones around olivine, with hypersthene in the inner zone facing the olivine. As stated above (Vol. XXIX, pp. 645-49) we are dealing here, however, with a reaction in the *solid* face between olivine and plagioclase at a maximum temperature of about 1250° - 1200° and generally somewhat lower—thus at least 300° lower than the temperature (1557°) at which, under a pressure of one atmosphere, olivine may crystallize from a melt of MgSiO_3 . The kelyphitic hypersthene zone next to the olivine may thus have nothing to do with the primary segregation of olivine from a melt of MgSiO_3 and the later transformation from olivine to orthopyroxene.

As maintained by Andersen (*loc. cit.* [1915], p. 453) the olivine, as a consequence of the splitting of MgSiO_3 , in the orthopyroxene-bearing igneous rocks, should in every case have crystallized earlier than the orthopyroxene, and the crystallization of the olivine should have been finished even before the beginning of the solidification of the orthopyroxene. But petrographic investigation of rocks rich in orthopyroxene but poor in olivine, shows that this is not so. We refer to the facts mentioned above (Fig. 25).

The conclusion from this is that bronzite and hypersthene, under high pressure, in the common deep-seated magmas (norites, etc.), crystallized directly from the magma in the same way as the other common silicate minerals. How it may be with enstatite in an almost pure MgSiO_3 magma, remains, however, an open question. In the igneous rocks, indeed, we never find orthopyroxene with less than *ca.* 7 per cent FeSiO_3 (or more than 93 per cent MgSiO_3).

C

1. Many minerals, such as olivine, monoclinic pyroxene, the feldspars, spinel, magnetite, etc., may be formed in melts at a pressure of one atmosphere, as well as in effusives and in deep-seated rocks—consequently at low, as well as at middle high, and very high pressure.

2. Some minerals, as *melilite* for instance, which crystallize out of melts at a pressure of one atmosphere, occur, moreover, in effusive rocks (melilite basalts, etc.) and in certain dike rocks (as

alnöite), but on the other hand are not—as yet (1920)—known from deep-seated rocks.

If we compare a number of analyses of troctolite (“forellenstein” and feldspar-peridotites) with for instance the analyses of slags given in my work “Silikatschmelzlös,” I, p. 16 (containing *ca.* 30–42 per cent SiO_2 , 8–28 per cent AlO_3 , 20–40 per cent CaO and up to 13 per cent MgO with some FeO , MnO , etc.), in which a melilite mineral (melilite-gehlenite) is crystallized, it is apparent that by re-melting at one atmosphere some of the deep-seated rocks mentioned, which consist only of olivine and anorthite-bytownite, they must recrystallize with more or less melilite besides several other minerals of which one is spinel (Vol. XXIX, p. 524).

Gehlenite occurs in some contact zones; it must consequently under certain conditions be formed at high pressure. And melilite occurs, as just mentioned, as a rarity in some dike rocks, which might have been solidified at a tolerably great depth, thus also at a tolerably great pressure.

It is worth noticing, however, that melilite, so far as known, is lacking in the common deep-seated rocks, and especially that, instead of a melilite mineral, we find in the troctolites the combination olivine and anorthite-bytownite.

A similar case is that of *leucite* which can crystallize in melts at a pressure of one atmosphere, and which occurs in many effusive and some dike rocks, but has only rarely been found in deep-seated rocks. When microcline and biotite are melted together in certain proportions, leucite results. And in many deep-seated rocks which by re-melting at one atmosphere would give leucite, we find instead of leucite other minerals, as microcline, biotite, etc.

3. On the other hand there are some minerals which in part preferentially and in part exclusively belong to deep-seated or other rocks formed at a very high pressure. As an instance we may choose *garnet*.

By re-melting garnet there results, as is known, not this mineral, but a mixture of other minerals, according to the composition of the garnet—melilite, anorthite, olivine, spinel, etc. On the other hand, we may get garnet by using certain chlorides, for instance AlCl_3 , as the solution medium. Garnet—or at least some varieties

of garnet—may thus also be formed under high temperature at the pressure of one atmosphere.

Garnet occurs as a primary formation in some effusives and often in various deep-seated rocks. The mineral further is formed as known *inter alia* by contact-metamorphism and by intensive dynamo-metamorphism.

Amphibole, as is known, does not crystallize from anhydrous silicate melts at one atmosphere but it is generally supposed to be conditioned by high pressure. This depends rather certainly on the fact that the magmas only at high pressure may carry the sufficient quantity of water (or hydroxyl) which seems to be a constitutional component of amphibole.

Biotite has, as is known, been produced synthetically by melting with fluorides, and the magnesia-mica *phlogopite* has also been established as crystallized out of common anhydrous slags containing a little fluorine.¹ Phlogopite may thus be formed by crystallization of silicate melts at a pressure of one atmosphere. But common mica occurs in the igneous rocks preferentially in deep-seated rocks; it occurs also, however, in effusives. On the other hand, muscovite never occurs as a primary mineral in effusives, but occurs in certain granites and especially in granite-pegmatite dikes.

As we shall show later, in granites of exactly the same composition—excluding the original content of H₂O, etc.—hypersthene, biotite or muscovite may crystallize. Which of these three minerals is formed, may depend on the content of H₂O, etc., in the magma (when least, hypersthene is formed; when most, muscovite).

¹ See my cited treatises from 1884-85 and 1888-90. In slags from the Kafveltorp copper works (containing 41-46 per cent SiO₂, 8-11 Al₂O₃, 7-15 FeO including *ca.* 0.5 Fe₂O₃, 13-20 CaO, 10-18 MgO, a little ZnO, Cu₂S, etc., also 3-5 K₂O+Na₂O and a little F) there has crystallized 10-15 per cent mica, in great leaves up to 5-6 mm. in diameter, with the following characteristics: pseudo-hexagonal thin leaves, with just as good cleavage as natural mica; elastic flexible; pressure figure as in natural mica; prism angle *ca.* 121°; optical biaxial and negative; acute bisectrix almost perpendicular on 001, differing only by 1-1.5°; 2 V only a very few degrees; colorless; very vivid interference colors; very resistant to acids; chemical composition: 42.20 SiO₂, 11.30 Al₂O₃, 5.92 FeO (with a little Fe₂O₃), 22.93 MgO, 2.29 CaO, 1.40 ZnO, 0.33 Cu₂S (mechanical), total 86.37 per cent, rest *ca.* 13 per cent K₂O, Na₂O and F. The mineral is thus a MgO-mica rather poor in FeO and Fe₂O₃, viz., a phlogopite, whose content of H₂O (or HO) is replaced by another component, F.

The influence of pressure with regard to the minerals amphibole, biotite, and muscovite must then be indirect, since the formation of these minerals depends essentially on the magmatic content of H_2O , etc., which further, to a certain extent, depends on the pressure.

By great differences in pressure, H_2O content, etc., a magma otherwise of the same or almost the same chemical composition may give rise to the crystallization of totally different minerals or combination of minerals. P. Niggli, in his work (1920, p. 207) cited below, mentions as a typical instance of this the two rocks, (1) a durbachite (rich in biotite and hornblende and further orthoclase, plagioclase, a little quartz and titanite bearing boundary facies of granite), and (2) a glassy leucite basalt.

	1. Durbachite	2. Leucitebasalt
SiO_2	51.05	51.43
TiO_2	1.76	1.12
Al_2O_3	14.49	14.88
Fe_2O_3	4.16	6.30
FeO	4.37	3.14
MgO	8.16	6.67
CaO	5.11	5.01
Na_2O	1.85	1.83
K_2O	7.25	9.22
P_2O_5	0.70	0.51
H_2O	1.05	0.74
Total	99.94	100.85

1. Durbachite from Durbach, Schwarzwald. A. Sauer, *Mitt. Badische Geol. Landesanst.*, II, 1892 (1890). 2. Leucitebasalt from Gaussberg, Kaiser Wilhelm II Land. R. Reinisch, *Deutsche Südpol-Exposition II* (1), 1906.

Undoubtedly, on account of the high content of water, biotite and hornblende, and further orthoclase, have been formed in the durbachite, while on the other hand in leucite basalt which solidified at lower pressure leucite was formed instead of orthoclase and K_2O -rich biotite.

RS dissolved in silicate melts crystallizes at a pressure of one atmosphere as monosulphid (oldhamite, alabandine, sphalerite, pyrrhotine or troilite, etc.), but may at high pressure by pneumatolytic processes (in the crystallization of magmas as described by Brögger¹

¹ *Zeits. f. Kryst. Min.*, XVI (1890), I, p. 161.

for the nepheline syenite-pegmatite dikes, further in contact zones, etc.), give rise to the formation of helvine (and danalite). At a moderately high pressure also some double-compounds of silicate and NaCl or Na₂SO₄ (sodalite, nosean and h  uyn) crystallize. But these minerals—and according to my experience this is also true of scapolite—may not be reproduced by melting the respective silicate with admixture of NaCl or Na₂SO₄ at common low pressure.

In this connection it may be further mentioned that the magmatic crystallization of minerals as FeS₂ and CaCO₃ imply a high pressure.

This review proves that the formation of many minerals, or combinations of minerals, may take place at low pressure as well as at moderately high or very high pressure, and further, that the *determinations undertaken at one atmosphere pressure in regard to the eutectics and mix-crystal systems, so far as these minerals are concerned, may also be made valid with only slight corrections at high pressures, even at the high pressure prevailing during the crystallization of the deep-seated magmas.*

But this may not be applied to all minerals, or combinations of minerals. The formation of some minerals, as melilite and leucite, is favored by low pressure; the formation of other minerals, as garnet, is favored by high pressure. For some minerals, as especially muscovite, further H₂O-bearing biotite and hornblende, a more or less high pressure may be an indispensable condition for crystallization from the magma; indeed indirectly depending on the fact that the presence of sufficient H₂O in the magma implies a high pressure. For pyrite and calcspar, which at one atmosphere are dissociated by moderate heating, high pressure is necessary for their crystallization from the magma.

It is to be noted that *garnet* has a much *higher* density (Mg-Al₂-garnet 3.7–3.8, Ca-Al₂-garnet 3.9–4.0, Ca-Fe₂-garnet 3.8–4.1, etc.) than the combination of those minerals which result from re-melting it at one atmosphere. On the other hand, *leucite* has a much *lower* density (2.45–2.50) than the combination of those minerals, especially orthoclase (2.55) and the various K₂O-rich micas (2.76–3.0) which generally replace leucite in the deep-seated magmas. And *melilite* (2.90–2.93) has somewhat *lower* density than the combina-

tion of a medium mixture principally of olivine (3.22) and anorthite (2.765) which in most cases replace it in the deep-seated rocks.

In all of these three cases we thus observe the fact that a combination of minerals, respectively a single mineral (leucite, melillite) in the effusives are replaced in the deep-seated rocks by a single mineral (garnet), respectively a combination of minerals, characterized by *increased* density.

This recalls the well known "volume law" valid for dynamo-metamorphism, viz., that various minerals under high pressure form new combinations with the minimum total volume—a law whose physicochemical cause, moreover, is not exactly elucidated.

Since the above section, in the main, was written, in the winter 1919–20, a treatise on "The Mineral Facies of Rocks," by P. Eskola,¹ was published, wherein he tries to establish some (five) facies for the mineral combinations depending on the pressure not only for the metamorphic, but also for the igneous rocks. Eskola classes with the last, the facies of the igneous rocks formed under the highest pressure, among others those especially investigated by him, namely garnet-rich (with up to 75 mol. per cent pyrop-component $\text{Mg}_3\text{Al}_2\text{SiO}_3\text{O}_{12}$) eclogites, which "occupy a volume about 15 per cent smaller than that of the corresponding gabbros." Eskola thus maintains the same views as those I have pointed out above. I call attention to this treatise, in which are given some new instances of the interdependence of the formation of certain mineral combination in the igneous rocks upon the pressure. Further on Eskola treats of the interdependence of the metamorphic new-formations upon the pressure, which matter I do not touch in this treatise.

[To be continued]

¹ *Norsk geol. Tidsskrift*, Vol. VI (1920).